

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 27/138, 27/128, 27/122, 27/08, 27/10		A1	(11) International Publication Number: WO 95/26815 (43) International Publication Date: 12 October 1995 (12.10.95)
(21) International Application Number: PCT/US95/03861		(81) Designated States: AU, BR, CA, CN, JP, MX, RU, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 29 March 1995 (29.03.95)		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data: 221,201 31 March 1994 (31.03.94) US			
(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).			
(72) Inventors: CHEN, Frank, Joung-yei; 28 Ellison Avenue, Edison, NJ 08820 (US). LE DEORE, Christophe; 508 Cinder Road, Edison, NJ 08820 (US). SPITZ, Roger; Rue des Fleurs, F-69360 Serezin (FR). LENACK, Alain, Louis, Pierre; 16, rue de la République, F-76000 Rouen (FR).			
(74) Agent: COHEN, Harvey, L.; Exxon Chemical Company, P.O. Box 710, Linden, NJ 07036 (US).			
(54) Title: SUPPORTED LEWIS ACID CATALYSTS FOR HYDROCARBON CONVERSION REACTIONS			
(57) Abstract			
A supported Lewis acid catalyst system effective for hydrocarbon conversion reactions including cationic polymerization, alkylation, isomerization and cracking reactions and comprising at least one Lewis acid immobilized on an anhydrous dihalide of Cd, Fe, Co, Ni, Mn or Mg is disclosed.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

SUPPORTED LEWIS ACID CATALYSTS FOR
HYDROCARBON CONVERSION REACTIONS

5 Technical Field

This invention relates to supported Lewis acid catalyst systems, to processes for preparing the catalyst systems, and to various hydrocarbon conversion reactions which are performed in the presence of such catalyst systems. More particularly, the invention relates to effective catalyst systems 10 for cationic polymerization, alkylation, isomerization and cracking reactions comprising at least one Lewis acid supported on an anhydrous dihalide of Cd, Fe, Co, Ni, Mn or Mg.

Background of the Invention

15 It is known to prepare metal halide catalysts for hydrocarbon conversion processes including the polymerization or alkylation of hydrocarbons. For example, it is disclosed in British patent 1,091,083 that metal halide polymerization and alkylation catalysts may be prepared by grinding anhydrous dihalides of Cd, Fe, Co, Ni, Mn or Mg to particles having a surface 20 area of 2-60 m²/g, while avoiding rehydration. This British patent further discloses that aluminum trialkyls or aluminum alkyl halide may be used as co-catalysts in conjunction with the anhydrous metal dihalides.

25 Lewis acids are among the most powerful initiators for hydrocarbon conversion reactions. Such catalysts have been used in liquid, gaseous and solid form, and have been supported or immobilized on various polymeric and inorganic substrates, including, for example, silica gel, alumina, graphite and various clays.

30 Both supported and unsupported Lewis acid catalysts have been used with varying degrees of success for initiating alkylation reactions and the carbocationic polymerization of olefins, such as isobutene. However, in spite of the advances made in the fields of alkylation and polymerization catalysis, there has been a continuous search for highly efficient catalyst systems which can be recycled or reused in cationic polymerization and alkylation processes. The present invention was developed pursuant to this search.

Summary of the Invention

In accordance with one aspect of the present invention, there is provided a supported Lewis acid catalyst system which is active for various hydrocarbon conversion reactions, including, in particular, carbocationic olefin polymerizations, alkylation, isomerization and cracking reactions. According to this aspect, the supported catalyst system is in the form of a particulate magnesium halide substrate on which there is supported or immobilized at least one Lewis acid, such as an aluminum halide or an alkyl aluminum halide.

10 In another aspect, a supported Lewis acid catalyst system is prepared by cogrinding an anhydrous magnesium halide, such as magnesium chloride, together with a Lewis acid, such as aluminum chloride, and a porogen (solid hydrocarbon, such as adamantane, whereafter the porogen is washed out by means of a suitable solvent and the supported catalyst is recovered.

15 In yet another aspect, a supported Lewis acid catalyst is prepared by first grinding an anhydrous magnesium halide, such as magnesium chloride, together with a porogen, followed by the addition of a solution of a Lewis acid, such as aluminum chloride, in toluene. Then, after allowing the resulting mixture to stand for about one day at about 100° to about 120°C., the product

20 mixture is washed several times with toluene to remove any free aluminum chloride. Then, after removing toluene under vacuum, the resulting supported Lewis acid catalyst is recovered as a powder.

Another aspect of the present invention provides a process for using the above supported Lewis acid catalyst systems. In a preferred embodiment of this aspect, there is provided a process for polymerizing a variety of monomers into homopolymers and copolymers, e.g., polyalkenes, by contacting the monomers with the supported Lewis acid catalyst system of this invention under carbocationic polymerization conditions. The monomers which may be used according to this aspect of the invention include those having

25 unsaturation which are conventionally polymerizable using carbocationic Lewis acid catalyst polymerization techniques, such as, for example, olefins characterized by the presence in their structure of the group $>\text{C}=\text{CH}_2$. To effect the process, at least one inlet stream comprising monomer feed to be polymerized is fed to a reactor having at least one discharge stream. The

30 monomer stream is polymerized in the reactor in the presence of the above-

35

- 3 -

described supported Lewis acid catalyst system. The resulting polymerized polymer is removed from the reactor along with the unreacted monomers in the discharge stream while the catalyst system is retained in the reactor.

In still other aspects, the catalyst systems of this invention may be used
5 in isomerization, cracking and alkylation processes. As is known in the art, alkylation may be simply described as the addition or insertion of an alkyl group into a substrate molecule. Of particular interest is the alkylation of aromatic and hydroxy aromatic substrates, such as benzene, toluene, xylene and phenol. Suitable alkylating agents include, for example, olefins, alkanes,
10 alkyl halides and mixtures. However, particularly preferred alkylating agents for use in the present invention include olefin oligomers, such as propylene oligomers, having from about 6 to about 50 carbon atoms and having one double bond per molecule.

A significant advantage of the present catalyst systems is that they are
15 stable and do not leach or otherwise deposit free Lewis acid into the reaction medium or, more importantly, into the reaction products. Another advantage is that the present catalyst systems are usable for multiple polymerization or alkylation cycles (in the context of a batch process) without regeneration, resulting in substantial cost savings, as well as the elimination of significant
20 amounts of hazardous waste typically generated in conventional Lewis acid processes. Not only can the Lewis acid catalyst systems of the present invention be employed for multiple cycles of polymerization, alkylation, isomerization and cracking, or on a continuous basis for extended times of polymerization, alkylation, isomerization and cracking, but they can also be
25 recovered readily from the polymerization and alkylation products by simple filtration techniques.

Detailed Description of the Preferred Embodiments

The novel supported Lewis acid catalyst systems of the present
30 invention may be prepared by fixing or immobilizing at least one Lewis acid on a suitably treated magnesium halide substrate.

For the purposes of this invention the terms fixed and immobilized are used interchangeably and are defined as wherein substantially all of the Lewis acid is incorporated in the layer of the magnesium halide support. In other
35 words, the Lewis acid is not readily extracted by a solvent or diluent under conditions of polymerization or alkylation.

- 4 -

Among the Lewis acids which are contemplated for use in this invention, there may be included the halides of aluminum, the halides of boron and the halides and alkyl halides of zinc. Preferred Lewis acids include, for example, aluminum halide where the halogen is independently selected from the group 5 consisting of fluorine, chlorine, bromine and iodine. Non-limiting examples of such preferred Lewis acids include aluminum and zinc chloride and mixtures thereof.

The substrates on which the Lewis acids may be supported include those anhydrous substrates having the formula MX_2 , where M is selected from 10 Cd, Fe, Co, Ni, Mn and Mg, and X is a halide. These substrates are sometimes referred as the family of "cadmium chloride layer" structures. Among the more preferred substrates are the magnesium dihalides, such as magnesium dichloride, magnesium dibromide, magnesium difluoride and magnesium diiodide; mixtures of such metal supports can also be used. 15 Magnesium dichloride is the most preferred substrate.

The Lewis acids may be supported on the magnesium halide substrate by any suitable technique. However, it has been found that particularly suitable catalyst systems are obtained when the Lewis acids are supported or fixed to the magnesium substrate by either of two preferred methods. In the 20 first preferred method, sometimes referred to herein as the cogrinding method, anhydrous magnesium halide, preferably magnesium chloride, and at least one Lewis acid, preferably $AlCl_3$, are coground, together with a porogen (solid hydrocarbon) in an oscillating ball mill. The cogrinding is performed at room temperature for a period of from about 1 hour to about 10 hours, typically 25 from about 4 to 6 hours.

In the second preferred method, sometimes referred to herein as the solution impregnation method, anhydrous magnesium halide, preferably magnesium chloride, is first ground in the oscillating ball mill in the presence of the porogen. Other methods known in the art can be used to prepare the 30 $MgCl_2$ support in order to generate porosity and make it useful for the purposes of this invention. Such methods are generally known in the Ziegler-Natta catalyst art, including, e.g., the use of H_2O and $SOCl_2$ and the use of H_2O in a thermal treatment at 200°C in the presence of HCl. Following the preparation of the $MgCl_2$, a solution of a Lewis acid, preferably $AlCl_3$ in 35 toluene, is added and allowed to mix for about 1 hours to about 2 days at room temperature, or preferably at an elevated temperature on the order of 80° to about 140°C., typically from about 100° to about 120°C for suitably adjusted

- 5 -

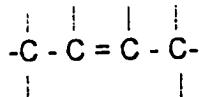
periods of time. The resulting mixture is then washed several times with toluene to remove any free $AlCl_3$, toluene solvent is removed under vacuum, and the resulting supported catalyst system is recovered as a powder.

As indicated above, both in the cogrinding method and in the solution impregnation method, it is preferable to grind the magnesium chloride substrate in the presence of the porogen. While the exact mechanism is not completely understood, and not wishing to be bound by any speculation, it is believed that grinding the magnesium chloride substrate in the presence of the porogen results in surface defects being formed in the magnesium chloride crystal lattice, which defects somehow provide sites where the $AlCl_3$ may become firmly bonded to the magnesium chloride substrate. The porogen (solid hydrocarbon) materials which are contemplated for use in this invention include, but are not limited to adamantane and solid hydrocarbon polymers which can be dissolved and washed away by means of suitable solvents. A large number of porogen materials which are useful for activating magnesium halides, such as magnesium chloride, are disclosed in the patent literature dealing with Ziegler-Natta catalysis. The choice of porogen is limited only to the extent that it must not react adversely with the Lewis acid components of the catalyst. It is the objective of such treatment of the substrate to increase the specific surface area to greater than about $20\text{ m}^2/\text{g}$; preferably greater than $50\text{ m}^2/\text{g}$; most preferably greater than $100\text{ m}^2/\text{g}$.

The novel immobilized catalysts of the present invention can be used to polymerize a variety of monomers into homopolymers and copolymers, e.g., polyalkenes. The monomers include those having unsaturation which are conventionally polymerizable using carbocationic Lewis acid catalyst polymerization techniques, and monomers which are the equivalents thereof. The terms cationic and carbocationic are used interchangeably herein. Olefin monomers useful in the practice of the present invention are polymerizable olefin monomers characterized by the presence of one or more ethylenically unsaturated groups. The monomers can be straight or branched monoolefinic monomers, such as vinyl ethers, ethylene, propylene, 1-butene, isobutylene, and 1-octene, or cyclic or acyclic conjugated or non-conjugated dienes.

Suitable olefin monomers are preferably polymerizable terminal olefins; that is, olefins characterized by the presence in their structure of the group $>C=CH_2$. However, polymerizable internal olefin monomers (sometimes referred to in the patent literature as medial olefins) characterized by the presence within their structure of the group:

- 6 -



5

can also be used to form polymer products. When internal olefin monomers are employed, they normally will be employed with terminal olefins to produce polyalkenes which are interpolymers. For purposes of the invention, when a particular polymerized olefin monomer can be classified as both a terminal 10 olefin and an internal olefin, it will be deemed to be a terminal olefin. Thus, 1,3-pentadiene (i.e., piperylene) is deemed to be a terminal olefin for purposes of this invention.

Preferred monomers used in the method for forming a polymer in accordance with the present invention are preferably selected from the group 15 consisting of alpha-olefins and typically C₃-C₂₅ alpha olefins. Suitable alpha-olefins may be branched or straight chain, cyclic, and aromatic substituted or unsubstituted, and are preferably C₃-C₁₆ alpha-olefins. Mixed olefins can be used (e.g., mixed butenes).

The alpha-olefins, when substituted, may be directly aromatic 20 substituted on the 2-carbon position (e.g., monomers such as CH₂=CH-C₆H₅ may be employed). Representative of such monomers include styrene, and derivatives such as alpha-methyl styrene, para-methyl styrene, vinyl toluene and its isomers.

In addition, substituted alpha-olefins include compounds of the formula 25 H₂C=CH-R³-X² wherein R³ represents C₁ to C₂₂ alkyl, preferably C₁ to C₁₀ alkyl, and X² represents a substituent on R³ and can be aryl, alkaryl, or cycloalkyl. Exemplary of such X² substituents are aryl of 6 to 10 carbon atoms (e.g., phenyl, naphthyl and the like), cycloalkyl of 3 to 12 carbon atoms (e.g., cyclopropyl, cyclobutyl, cyclohexyl, cyclooctyl, cyclodecyl, cyclododecyl, and the like) and alkaryl of 7 to 15 carbon atoms (e.g., tolyl, xylyl, ethylphenyl, diethylphenyl, ethynaphthyl, and the like). Also useful are bicyclic, substituted 30 or unsubstituted olefins, such as indene and derivatives, and bridged alpha-olefins of which C₁-C₉ alkyl substituted norbornenes are preferred (e.g., 5-methyl-2-norbornene, 5-ethyl-2-norbornene, 5-(2'-ethylhexyl)-2-norbornene, and the like).

- 7 -

Illustrative non-limiting examples of preferred alpha-olefins are propylene, 1-butene, isobutene, 1-pentene, 1-hexene, 1-octene, and 1-dodecene.

Dienes suitable for purposes of this invention include straight chain, 5 hydrocarbon diolefins or cycloalkenyl-substituted alkenes having about 6 to about 15 carbon atoms, including, for example, 1,4-hexadiene, 5-methyl-1,4-hexadiene, 1,3-cyclopentadiene, tetrahydroindene, dicyclopentadiene, 5-methylene-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene, allyl cyclohexene and vinyl cyclododecene.

10 Of the non-conjugated dienes typically used, the preferred dienes are dicyclopentadiene, methyl cyclopentadiene dimer, 1,4-hexadiene, 5-methylene-2-norbornene, and 5-ethylidene-2-norbornene. Particularly preferred diolefins are 5-ethylidene-2-norbornene and 1,4-hexadiene.

15 The polymers and copolymers which can be manufactured by the process of the present invention are those which can be manufactured by a carbocationic polymerization process and include but are not limited to polyalkenes, such as polyisobutene, poly(1-butene), polystyrene, isobutene styrene copolymers, and the like. The term copolymer as used herein is defined to mean a polymer comprising at least two different monomer units.

20 In particular, the immobilized catalysts of the present invention are especially useful for manufacturing polyisobutene and poly(1-butene) from feedstreams containing butene monomers. It is especially preferred to use refinery feed streams containing C₄ monomers, commonly referred to as Raffinate I and Raffinate II.

25 The carbocationic polymerization process of the present invention may be carried out in a polar or, preferably, non-polar reaction medium as a continuous, semi-continuous or batch process. Suitable polar solvents which may be used as the polymerization reaction medium include, for example, methyl chloride, dichloromethane, ethyl chloride or nitromethane or the like, 30 whereas suitable non-polar solvents include, for example, carbon tetrachloride, hexane, heptane, cyclohexane, and more generally the linear or branched, saturated or unsaturated hydrocarbon solvents which can be found in the stream of monomers obtained from various cracking processes.

35 The reactors which may be utilized in the practice of the present invention include conventional reactors and equivalents thereof such as batch reactors, stirred tank reactors, fluidized bed reactors, and continuous tank or tubular reactors and the like.

- 8 -

The reactor will contain sufficient amounts of the immobilized catalyst system of the present invention effective to catalyze the polymerization of the monomer containing feedstream such that a sufficient amount of polymer having desired characteristics is produced. The reaction conditions will be 5 such that sufficient temperature, pressure and residence time are maintained effective to maintain the reaction medium in the liquid state and to produce the desired polymers having the desired characteristics.

Typically, the catalyst to monomer ratio utilized will be those conventional in this art for carbocationic polymerization processes. For 10 example, catalyst to monomer mole ratios will typically be about 1/5000 to about 1/50, more typically about 1/1000 to about 1/100, and preferably about 1/500 to about 1/200. This mole ratio will be calculated by determining the number of Lewis acid catalyst sites in the immobilized Lewis acid catalyst. This can be done by using conventional analytic testing techniques such as 15 elemental analysis, NMR (e.g., aluminum NMR) and absorption spectroscopy. Once the number of Lewis acid sites per unit of immobilized catalyst is known, the mole ratio is calculated in a conventional manner.

The polymerization reaction temperature is conveniently selected based on the target polymer molecular weight and the monomer to be polymerized as 20 well as standard process variable and economic considerations, e.g., rate, temperature control, etc. Typically temperatures from about -100°C to about +75°C are useful in the process; more typically about -50°C to about +50°C, depending, as noted above, on polymer molecular weight. Reaction pressure will typically be about 200 kPa to about 1600 kPa, more typically about 300 to 25 about 1200 kPa, and preferably about 400 to about 1000.

The monomer feedstream to this process may be at least one pure or mixed monomer feedstream or combinations thereof. Preferably, the monomer feedstream may be mixed with solvents such as hexane or heptane, and the like. A preferred feedstream to this process may be a pure or mixed refinery 30 butene stream containing one or more of 1-butene, 2-butene, (cis and trans), and isobutene. The preferred feedstreams (preferred on an availability and economic basis) are available from refinery catalytic crackers and steam crackers. These processes are known in the art. The butene streams typically contain between about 6 wt.% to about 50 wt.% isobutylene together with 1- 35 butene, cis- and trans-2-butene, isobutane and less than about 1 wt.% butadiene. One particularly preferred C₄ feedstream is derived from refinery catalytic or steam cracking processes and contains about 6-45 wt.%

- 9 -

isobutylene, about 25-35 wt.% saturated butanes and about 15-50 wt.% 1- and 2-butenes. Another preferred C₄ feedstream is referred to as Raffinate II characterized by less than about 6 wt.% isobutylene.

5 The monomer feedstream is preferably substantially anhydrous, that is, it contains less than 50 ppm, and more preferably less than about 30 ppm, and most preferably less than about 10 ppm, by weight of water. Such low levels of water can be obtained by contacting the feedstream, prior to the reactor, with a water absorbent (such as NaH, CaCl₂, CaSO₄, molecular sieves and the like) or by the use of distillation drying.

10 The monomer feedstream is typically substantially free of any impurity which is adversely reactive with the catalyst under the polymerization conditions. For example, the monomer feed preferably should be substantially free of bases (such as caustic), sulfur-containing compounds (such as H₂S, COS, and organo-mercaptans, e.g., methyl mercaptan, ethyl mercaptan), N-containing compounds, and the like.

15 The monomer feedstream is typically substantially free of aromatic compounds to avoid alkylation reactions. Therefore, use of an aromatic solvent generally is not envisioned in this polymerization process.

20 A material acting as a cocatalyst (or promoter) may optionally be added to a monomer feedstream before that feed is introduced to a reactor or it may be added separately to the reactor, e.g., to the catalyst bed. A variety of conventional cocatalysts or equivalents can be used including inorganic acids such as hydrogen halides, lower alcohols, C₂-C₂₄ secondary or tertiary alkyl halides, organic acids such as carboxylic acids and sulfonic acids, and the like.

25 For example, gaseous, anhydrous HCl, may be employed as a cocatalyst. The HCl will be employed in a catalytically effective amount, which amount will generally range from about 50 to 5,000 ppm by weight of the monomer feed, preferably 50 to 500 ppm (e.g., 70 to 200 ppm) by weight of the monomer feed when the monomer feed comprises >5 wt.% isobutylene, and preferably from about 100-5,000 ppm (e.g., 400-3,000 ppm) by weight when the feed comprises n-butenes and <5 wt.% isobutylene. If anhydrous HCl is added to the feedstream containing isobutene, t-butyl chloride is formed before contact with the solid catalyst.

30

35 The order of contacting the monomer feedstream, catalyst, cocatalyst (if any), and solvent is not critical to this invention. Accordingly, the catalyst and cocatalyst can be added to the reactor before or after adding the monomer feedstream and solvent. Alternatively, the catalyst and monomer feedstream

- 10 -

can be added before or after adding the cocatalyst and solvent.

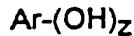
The degree of polymerization of polymers (and oligomers) produced with the catalyst of this invention will be determined by the desired end use. Typically the degree of polymerization is from about 5 to 5,000; more typically 5 from about 10 to about 1,000; for lower molecular weight polymers and oligomers the degree of polymerization will typically be about 5 to about 100. Correspondingly, the number average molecular weight, M_N , of a polymeric product will be determined by the monomer and degree of polymerization; for a C₄-based polymer typical values are from about 300 to about 300,000 10 gm/mole, depending on the intended end use of the product. Number average molecular weight is conveniently measured by a suitably calibrated gel permeation chromatography (GPC) instrument. The polydispersity index (PDI) of the polymer, also known as the molecular weight distribution (M_W/M_N), will typically range from about 4 to about 25, more typically about 5 to about 22, 15 and preferably about 6 to about 20.

Lewis acid catalysts of the present invention also find use in other hydrocarbon conversion processes including alkylation, isomerization and cracking. For example, the catalysts may be employed in the cracking of long chain hydrocarbons, e.g., heptane, butane, etc., to produce shorter chain 20 products such as ethane, propane, butanes, etc. Additionally, the catalysts may be used to catalyze the isomerization of normal alkanes to their branched chain isomers.

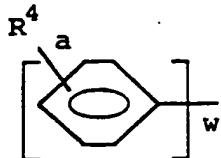
The alkylation process of the present invention will be conducted by contacting the aromatic or hydroxy aromatic substrate and alkylating agent 25 under reaction conditions, including mole ratio, temperature, time and catalyst ratio sufficient to alkylate the substrate.

The hydroxy aromatic substrate compounds useful in the preparation of the alkylated materials of this invention include those compounds having the formula:

30



wherein Ar represents



- 11 -

and z is an integer from 1 to 2, w is an integer from 1-3, a is 1 or 2 and R⁴ is a C₁-C₂₄ alkyl radical.

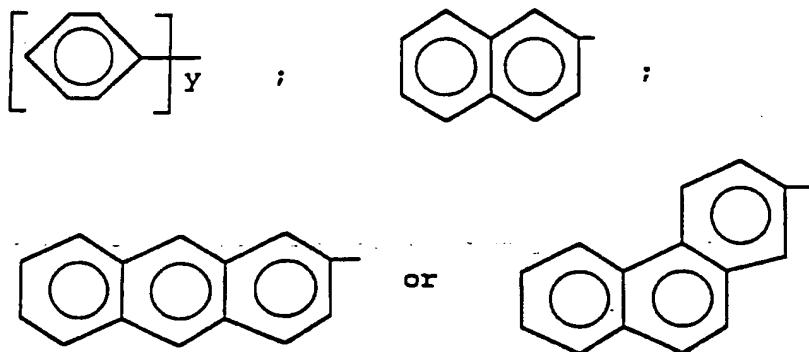
Illustrative of such Ar groups are phenylene, biphenylene, naphthalene and the like.

5 The aromatic substrate compounds useful in the preparation of the alkylated materials of this invention include those compounds having the formulas:



10

wherein Ar¹ represents:



15

wherein b is one or two; R⁵ is C₁-C₂₄ alkyl, C₃-C₂₄ cycloalkyl, C₆-C₁₈ aryl, C₇-C₃₀ alkylaryl, OH, or H; and y is 1-3.

Illustrative of such Ar¹ groups are benzene, phenylene, biphenylene, naphthalene, and anthracene.

20

The substrate generally will be contacted in a molar ratio of from about 0.1 to 10 preferably from about 1 to 7, more preferably from about 2 to 5, moles of the substrate per mole of the alkylating agent. Conventional ratios of alkylating agent typically will be used. The ratio typically will be about 0.5 to 2:1, more typically about 0.8 to about 1.5:1, and preferably about 0.9 to about 1.2:1.

25 The selected catalyst can be employed in widely varying concentrations. Generally, the catalyst will be charged to provide at least about 0.001, preferably from about 0.01 to 0.5, more preferably from about 0.1 to 0.3, moles of Lewis acid catalyst per mole of substrate charged to the alkylation reaction zone. Use of greater than 1 mole of the Lewis acid catalyst per mole of substrate is not generally required. The reactants can be contacted with the

30

- 12 -

present immobilized Lewis acid catalyst system employing any conventional solid-liquid contacting techniques, such as by passing the reactants through a fixed bed of catalyst particles. The upper limit on the moles of catalyst employed per mole of substrate compound is not critical.

5 The temperature for alkylation can also vary widely, and will typically range from about 10 to 250°C, preferably from about 20 to 150°C, more preferably from about 25 to 80°C.

10 The alkylation reaction time can vary and will generally be from about 1 to 5 hours, although longer or shorter times can also be employed. The alkylation process can be practiced in a batchwise, continuous or semicontinuous manner.

15 Alkylation processes of the above types are known and are described, for example, in U.S. Patents 3,539,633 and 3,649,229, the disclosures of which are hereby incorporated by reference.

20 The invention will be understood more fully in conjunction with the following examples which are merely illustrative of the principles and practice thereof. The invention is not intended to be limited by these illustrative examples. Parts and percentages where used are parts and percentages by weight, unless specifically noted otherwise.

Example 1: Catalyst Synthesis (Cogrinding)

25 A magnesium chloride supported aluminum chloride catalyst was prepared by cogrinding 5 g MgCl₂, 1.4 g AlCl₃ and 0.64 g adamantane (porogen) in a high speed ball mill equipped with a vertically oscillating grinding pot that was shaken with a frequency of 6 to 7 Hz with a maximum acceleration of 60 m.s⁻² over 6 cm. The grinding pot was built as a stainless steel Schlenck tube and was operated under an argon atmosphere to avoid contamination. The volume of the grinding pot was 80 cm³. The MgCl₂, AlCl₃ and adamantane were ground for 5 hours at room temperature. The resulting 30 powdered mixture was slurried in heptane to dissolve the adamantane and was then filtered to recover a wet powdered catalyst. The wet catalyst was then washed three times with heptane to remove any remaining adamantane and the resulting catalyst was dried at 100° C. under vacuum and recovered as a powder. The catalyst, which is referred to hereinbelow as Catalyst MgAl-1, 35 contained 4.3% Al and 20.1% Mg, giving a weight ration of Al:Mg of 0.21.

- 13 -

Example 2: Catalyst Synthesis (Cogrinding)

The procedure of Example was repeated, except that 3.2 g of $MgCl_2$, 5 g of $AlCl_3$ and 0.8 g of adamantane were fed to the ball mill. The resulting catalyst, which is referred to hereinbelow as Catalyst MgAl-2, was analyzed for 5 12.2% Al and 9.9% Mg, giving a weight ratio of Al:Mg of 1.23.

Example 3: Catalyst Synthesis (Impregnation)

Anhydrous $MgCl_2$ (6 g) and adamantane (0.6 g) were milled for 5 hours in accordance with the procedure of Example 1. The resulting mixture was 10 slurried in heptane and transferred under argon to a glass Schlenck flask. The slurry was filtered and washed three times in heptane to remove all of the adamantane. A solution of $AlCl_3$ in toluene was then added to the milled $MgCl_2$ and the resulting mixture was allowed to stand for one day at $110^\circ C$. The resulting product mixture was filtered, washed three times with toluene to 15 remove free $AlCl_3$, dried at $100^\circ C$. under vaccuum to remove the remaining toluene, and recovered as a powder. The catalyst, which is referred to hereinafter as Catalyst MgAl-3, was analyzed for 3.2% Al and 21.4% Mg, giving a ration of Al:Mg of 0.14.

20 Example 4: 1-Hexene Oligomerization

In a glass flask equipped with a thermometer, there were placed 10 ml of pure 1-hexene monomer (pure 1-hexene corresponds to 8 mol/l) and 150 mg of Catalyst MgAl-1. (Run 1). The monomer/catalyst mixture achieved 100% conversion of the 1-hexene to oligomer in 17 hours. The procedure was 25 repeated (Run 2), except that a small amount of HCl (0.7 mmol) was added to the reaction flask as a cocatalyst. The small amount of HCl cocatalyst did not have any apparent effect on the oligomerization reaction since 100% conversion was again achieved in about 17 hours. The procedure was again repeated in a comparative run (Run 3), except that an unsupported $AlCl_3$ 30 catalyst (45 mg) was used in place of MgAl-1. The unsupported catalyst resulted in only a 30% conversion of the 1-hexene in 17 hours. The oligohexenes of Runs 1 and 2 were tentatively charcterized by gas-liquid chromatography (GLC) and by gel permeation chromatography (GPC). The molecular weights of the products were determined on a Waters 35 chromatograph equipped with 4 columns of Micro-Styragel (10^4 , 10^3 , 500, and 100 \AA). The calibration was made using polystyrene standards. The number average molecular weight was determined to be 420 for the product of Run 1

- 14 -

and 340 for the product of Run 2 in polystyrene equivalent. From GLC chromatograms, it was estimated that the majority of the oligohexene product had peaks at about $D_p=5$ or 6. The results of this example are set forth in Table 1.

5

TABLE 1

Run	Hexene, mol/l	Catalyst, g/l	HCl, mmol	% Conv.	Time hr.
1	8	15	-	100	17
2	8	15	0.7	100	17
3	8	4.5	-	30	17

10 Example 5: 1-Hexene Oligomerization

The procedure of Example 4 was repeated, except that in several runs, t-butyl chloride (t-BuCl) in heptane was used as a cocatalyst. Each run was conducted with 10 ml of 1-hexene and conversions were calculated on the mass of unvolatile product after filtration on a filter paper and evaporation of heptane and unreacted 1-hexene. The results of this example are set forth in Table 2.

TABLE 2

Run	1-Hexene, ml	MgAl-1, g/l	t-BuCl, mol/l	% Conv.	Time, hr.
4	10	3	-	16	22.
5	10	2.6	0.14	82	0.25
6	10	1.3	0.2	63	0.25
7	10	2.3	0.05	45	0.25

20 The data in Table 2 clearly indicate that the use of a modestly higher amount of cocatalyst than was used in Run 2 of Example 4 resulted in significantly higher 1-hexene oligomerization conversion rates.

Example 6: 1-Hexene Oligomerization

25 The procedure of Example 5 was repeated, except that the Catalyst MgAl-1 was replaced with Catalyst MgAl-2 or with Catalyst MgAl-3. The results of this example are set forth in Table 3.

- 15 -

TABLE 3

Run	1-Hexene, ml	Catalyst, g/l	t-BuCl, mol/l	% Conv.	Time, min.
8	10	MgAl-2, 2	-	13	15
9	10	MgAl-2, 3.4	0.17	100	15
10	10	MgAl-3, 2.5	0.2	59	15
11	10	MgAl-3, 3.3	0.3	86	15

5

A comparison of the data in Tables 1, 2 and 3 indicates that the rate of 1-hexene conversion is higher when Catalyst MgAl-2 is used than when Catalyst MgAl-1 or unsupported AlCl_3 is used. The data also reflects the high conversion rates obtained when Catalyst MgAl-3 is used in conjunction with t-butyl chloride as a cocatalyst. The relatively higher conversion rates achieved using Catalyst MgAl-2 can be appreciated more fully by reference to Table 4 which compares the calculated activities of AlCl_3 , MgAl-1 and MgAl-2, expressed as the mass of polymer produced per mol of aluminum per minute.

15

TABLE 4

Run	Catalyst (Al, mM)	Polymer Mass, g	Time, min	Activity
1	MgAl-1, 24	6.7	1020	0.27
8	MgAl-2, 9	0.87	15	6.45
3	AlCl_3 , 33	2.01	1020	0.06

From the calculated activities in Table 4, it would appear that the activity (g Pol/mol Al/min) of MgAl-1 is about 4 times higher than that of AlCl_3 , and that 20 the activity of MgAl-2 is about 24 times than that of MgAl-1.

Example 7: 1-Butene Polymerization

In a glass flask equipped with a thermometer and a pressure transducer, there were placed 100 ml of heptane and the amount of 1-butene monomer indicated in Table 5. To this mixture, maintained at the indicated temperature, there was added the indicated amount of catalyst and cocatalyst. The contents of the flask were maintained at the indicated temperature for indicated period of time, whereafter the reaction was discontinued and the

- 16 -

reaction products were analyzed by GPC. The results of this example are set forth in Table 5.

TABLE 5

5

Run	1-Butene mol/l	Cat., g/l	t-BuCl, mol/l	Conv %	T, °C	Time hr.	M _n	M _w
12	2	MgAl-1, 1.7	-	5	16	2.0	-	-
13	2	MgAl-1, 2.2	0.2	80	35	0.25	830	1660
14	2	MgAl-2, 0.64	0.3	100	16-45	0.33	660	1070
15	2	MgAl-2, 0.64	-	60	70	5.0	1450	2800
16	2	MgAl-2, 0.64	-	30	70	2.0	1400	2670
17	1.6	MgAl-3, 0.6	0.06	45	40	3.0	-	-

The data in Table 5 (Run 12), indicates the advantage of using a cocatalyst (t-butyl chloride) in conjunction with the catalysts of this invention. More specifically, Run 1 resulted in only a 5% conversion in 2 hours when a 2 molar solution of 1-butene was polymerized at 16° C. in the presence of Catalyst MgAl-1, without the addition of a cocatalyst; whereas Run 13 resulted in an 80% conversion in only 15 minutes when 1-butene was polymerized at 35° C. using Catalyst MgAl-1 and t-butyl chloride as a cocatalyst.

15 Example 8: Toluene Alkylation

In a series of runs, toluene was alkylated using Catalyst MgAl-2 as the catalyst and 1-hexene (Runs 18-20), 1-butene (Run 21) or a mixture of straight chain alpha-olefins (Run 22) comprising 49% C₂₀, 41% C₂₂ and 8% C₂₄ alpha-olefins as the alkylating agent. The reaction products were analyzed by GLC and the percentage of alkylation products was estimated from peak areas displayed on the chromatograms. In the first alkylation run using 1-hexene as the alkylating agent (Run 18), the alkylation reaction took place very quickly as the reaction temperature increased from 20° C. to about 60° C. within a few seconds after the hexene was added to the toluene and catalyst. Accordingly, in the remaining runs in which 1-hexene was used as the alkylating agent (Runs 19 and 20), the 1-hexene was added dropwise to a suspension of the catalyst in toluene and reaction temperature was maintained at 0° C. by

- 17 -

placing the reaction flask in an ice bath. In all runs, the alkylation reaction was performed in the absence of any cocatalyst. The results of this example are set forth in Table 6.

With reference to Table 6, it can be seen that in all of the runs using 1-hexene as the alkylating agent, the conversion was almost 100% complete and only small traces of oligomerization products were detected. Also, except for Run 18, where the reaction took place very rapidly under uncontrolled temperature increase, even at high toluene/1-hexene ratios, dialkylated and trialkylated products were produced in non-negligible amounts.

10

TABLE 6

Run	MgAl-2, g/l	Alkylating Agent, mol	toluene, mol	M-D-T*	T, C°	Conv. %
18	1.30	1-hexene, 0.08	0.18	75-25-0	20-60	100
19	0.75	1-hexene, 0.15	0.38	65-20-14	0	100
20	1.55	1-hexene, 0.08	0.32	71-17-11	0	100
21	1.3	1-butene, 0.13	1.07	40-40-11	30	100
22	1.3	C ₂₀ -C ₂₄ olefins, 0.06	0.04	100-0-0	0	98

15 * M = % monoalkylated products; D = % dialkylated products; T = % trialkylated products

Example 9: Isobutylene Polymerization

In a glass flask were introduced 0.18 g of catalyst MgAl-1 prepared according to Example 1 and 100 ml of heptane. Starting at room temperature, isobutene is introduced in the reaction mixture by bubbling. The fast reaction increases the temperature of the reaction mixture up to a maximum of 50° C. The introduction of monomer is then stopped and the mixture is allowed to stir for 1/2 hour. The products are then recovered by filtration and after evaporation of solvent and unreacted monomer, 12 g of polymer having a $M_n=630$ and PDI=1.4, determined by GPC, is recovered.

CLAIMS:

1. A catalyst system effective for catalyzing hydrocarbon conversion reactions, comprising a catalyst support consisting essentially of at least one substrate having the formula MX_2 , where M is selected from the group consisting of Cd, Fe, Co, Ni, Mn and Mg, and X is a halogen independently selected from the group consisting of fluorine, bromine, chlorine and iodine; and at least one Lewis acid immobilized on said substrate, said catalyst system being free from titanium-, vanadium-, hafnium- and zirconium-containing Ziegler polymerization components.
2. The catalyst system according to Claim 1, wherein said Lewis acid is selected from the group consisting of aluminum halides, boron halides and zinc halides and zinc alkyl halides wherein said halogen is selected from the group consisting of fluorine, bromine, chlorine and iodine.
3. The catalyst system according to Claim 2, wherein said magnesium halide support comprises magnesium chloride.
4. The catalyst system according to any one of Claims 1 to 3, further comprising a porogen.
5. A process for preparing a catalyst system effective for hydrocarbon conversion reactions, wherein said catalyst system is free from titanium-, vanadium-, hafnium- and zirconium-containing Ziegler-type catalyst components, comprising:
 - (a) forming an admixture comprising (i) a magnesium halide, (ii) a porogen and (iii) at least one Lewis acid selected from the group consisting of aluminum halides, boron halides and zinc halides and zinc alkyl halides, wherein said halogen is selected from the group consisting of fluorine, bromine, chlorine and iodine;
 - (b) cogrinding said admixture;
 - (c) washing the coground admixture with a solvent for said porogen to remove said porogen therefrom; and
 - (d) recovering a powdered supported Lewis acid catalyst system.

- 19 -

6. The process according to Claim 5, wherein said Lewis acid is selected from the group consisting of aluminum halides, boron halides and zinc halides and zinc alkyl halides, wherein said halogen is selected from the group consisting of fluorine, bromine, chlorine and iodine.

7. A process for preparing a catalyst system effective for hydrocarbon conversion reactions, wherein said catalyst system is free from titanium-, vanadium-, hafnium- and zirconium-containing Ziegler-type catalyst components, comprising:

- (a) forming a porous magnesium halide;
- (b) adding to said porous component (a) a solution of at least one Lewis acid selected from the group consisting of aluminum halides, boron halides and zinc halides and zinc alkyl halides, wherein said halogen is selected from the group consisting of fluorine, bromine, chlorine and iodine;
- (c) washing the resulting mixture to remove any excess Lewis acid compound; and
- (d) recovering from said washed mixture a powdered, supported Lewis acid catalyst system.

8. The process according to Claim 7, wherein said Lewis acid is allowed to mix with said porous component at from about room temperature to about 140° C. for a period of from about 1 hours to about 2 days before said resulting mixture is washed in step (c); and wherein solvent is removed from said washed mixture in step (d) under vacuum.

9. A process for polymerizing olefin monomers, which comprises: contacting olefin monomer under cationic polymerization reaction conditions with a catalytically effective amount of a Lewis acid catalyst system, said catalyst system comprising a catalyst support consisting essentially of a magnesium halide and at least one Lewis acid selected from the group consisting of aluminum halides, boron halides and zinc halides and zinc alkyl halides, wherein said halogen is selected from the group consisting of fluorine, bromine, chlorine and iodine, fixed on said support, said catalyst being free from titanium-, vanadium-, hafnium- and zirconium-containing Ziegler-type catalyst components.

- 20 -

10. A cationically polymerized olefin polymer prepared in accordance with the process of Claim 9.

11. A process for alkylating an aromatic or hydroxy aromatic substrate, which comprises: contacting the substrate with an alkylating agent under alkylation conditions with a catalytically effective amount of a Lewis acid catalyst system, said catalyst system comprising a catalyst support consisting essentially of a magnesium halide and at least one Lewis acid selected from the group consisting of aluminum halides, boron halides and zinc halides and zinc alkyl halides, wherein said halogen is selected from the group consisting of fluorine, bromine, chlorine and iodine, fixed on said support, said catalyst system being free from titanium-, vanadium-, hafnium- and zirconium-containing Ziegler-type catalyst components.

12. The process according to any one of Claims 9 and 11, wherein said Lewis acid is selected from the group consisting of aluminum halides, boron halides and zinc halides and zinc alkyl halides, wherein said halogen is selected from the group consisting of fluorine, bromine, chlorine and iodine

13. In a hydrocarbon conversion process wherein at least one hydrocarbon is contacted with a conversion catalyst under conversion conditions, the improvement comprising contacting said hydrocarbon with the catalyst system of Claim 1.

14. The process of Claim 13 wherein said hydrocarbon conversion is isomerization.

15. The process of Claim 13 wherein said hydrocarbon conversion is cracking.

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 95/03861

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J27/138 B01J27/128 B01J27/122 B01J27/08 B01J27/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	EP,A,0 609 123 (ATOCHEM ELF SA) 3 August 1994 ---	
A	WO,A,90 08118 (BATTELLE MEMORIAL INSTITUTE) 26 July 1990 ---	
A	US,A,4 935 565 (HARLEY A DALE ET AL) 19 June 1990 ---	
A	FR,A,2 658 498 (ATOCHEM) 23 August 1991 ---	
A	US,A,5 019 652 (TAYLOR CHARLES E ET AL) 28 May 1991 -----	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

9 August 1995

Date of mailing of the international search report

16.08.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Thion, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/03861

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0609123	03-08-94	FR-A-	2700766	29-07-94
		AU-B-	5397094	18-08-94
		BR-A-	9400337	16-08-94
		CA-A-	2113510	28-07-94
		CN-A-	1101338	12-04-95
		JP-A-	6247884	06-09-94
-----	-----	-----	-----	-----
WO-A-9008118	26-07-90	AU-A-	4839990	13-08-90
		CA-A-	2005485	11-07-90
		JP-A-	2184641	19-07-90
		US-A-	5001290	19-03-91
-----	-----	-----	-----	-----
US-A-4935565	19-06-90	EP-A-	0443071	28-08-91
		US-A-	5041406	20-08-91
-----	-----	-----	-----	-----
FR-A-2658498	23-08-91	CN-A,B	1054404	11-09-91
		CN-A-	1097352	18-01-95
		EP-A-	0449673	02-10-91
		JP-A-	4228421	18-08-92
		US-A-	5212133	18-05-93
		US-A-	5346972	13-09-94
-----	-----	-----	-----	-----
US-A-5019652	28-05-91	US-A-	5139991	18-08-92
-----	-----	-----	-----	-----